

Characterization of the Intermediary Boundary Layer in Glass Ionomer Cement and at the Dental Enamel Surface: A Comparison of C(1s) NEXAFS and FT-IR Investigations

T. Schäfer, (Research Center Karlsruhe, INE), S. Willigeroth, R. Zimehl, G. Lagaly (C. Albrechts U., Kiel), S. Wirick, C. Jacobsen (SUNY, Stony Brook)

Beamline(s): X1A

Introduction: Intermediary boundary layer reactions of the major glass ionomer cement (GIC) components polyacrylic acid and vitreous body (Ca-Na-F-P-silicate) as well as the interaction between the dental enamel and GIC are not understood in detail. Structural studies using atomic force microscopy (AFM) revealed high resolution in-situ details on the edging process (1), but lack on chemical information. FT-IR studies are limited in spatial resolution to the μm scale (2,3). However, the combination with high resolution spectromicroscopy investigations using the scanning X-ray microscope at the C(1s) edge can elucidate the chemical reactions at these boundary layers.

Methods and Materials: A commercially available GIC (Aqua Cem, Voco, Cuxhaven) consisting of 74.4 wt % Ca-Na-F-P-Al-silicate and 24.8 % polyacrylic acid with a mean particle diameter of 5 μm was used to investigate the GIC intermediary boundary layer. Interaction between dental enamel and GIC was simulated by conditioning the dental enamel surface analogue hydroxyapatite (HAP, Fluka "high resolution, 50 μm mean particle size) with polyacrylic acid solution and room drying of the mixture. The hydroxyapatite particle size decreased during the conditioning step to approximately 10 μm . For reference spectra pure polyacrylic acid (Ketac conditioner) and hydroxylapatite (HAP, Fluka "high resolution) were used.

Results: FT-IR spectra of the GIC material revealed bands at 1705 cm^{-1} ($\nu(\text{C}=\text{O})$) typical for carboxyl groups and a shoulder at 1558 cm^{-1} ($\nu(\text{CO})$ in COO^-) indicating the presence of carboxylate binding. Comparable FT-IR results were obtained for the conditioned hydroxylapatite (1701 cm^{-1} , 1562 cm^{-1}). The C(1s) NEXAFS spectra of GIC and pure polyacrylic acid both showed a observable π^* resonance for C=C bonds (284.5 eV). Additionally the intensity of the C=C band increased in GIC, whereas the π^* resonances of C=O and C-H decreased. The C(1s) NEXAFS investigations reveal that the GIC material as well as the pure polyacrylic acid are not fully polymerized documented by the C=C band. Furthermore the polyacrylic acid in GIC show higher C=C and lower C=O functional group content and FT-IR spectroscopy indicate a chemisorption (carboxylate vibration band) of polyacrylic acid with Ca-Na-F-P-Al-silicate.

In the polyacrylic acid conditioned hydroxyapatite the intensity of the C=C band vanishes and a decrease in the carboxyl band (288.4 eV) is observable indicating a reduction of C=O bonds. The reduction in the C=O π^* resonance at 288.4 eV of conditioned hydroxyapatite compared to pure polyacrylic acid can be interpreted as a chemisorption of two equivalent C-O bonds on the hydroxyapatite surface.

Conclusions: The combination of FT-IR and C(1s) NEXAFS is a promising combination to elucidate chemical details on the intermediary boundary layer in the sub-micrometer range.

References: 1. Watari, F, *J. Electron Microscopy*, **48** (5), 537 (1999).

2. Bohic, S, Heymann, D, Pouëzat, J A, Gauthier, O, Daculsi, G., *Comptes Rendus de l'Academie Des Sciences. Serie III, Sciences de la Vie*, **321** (10), 865 (1998).

3. Sowa, M G, Mantsch, H H, *Calcified Tissue International*, **54** (6), 481 (1994).